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REACTIONS OF NICKEL—CARBENE COMPLEXES GENERATED FROM NICKELACYCLE COMPLEXES

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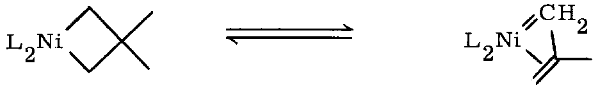
Summary: Nickel carbene species, generated from nickelacyclobutane complexes, reacted with hydrogen and carbon monoxide to give methane and ketene, respectively.

Recently, nickel-carbene complexes and nickelacyclobutane complexes have been suggested to be important intermediates for olefin metathesis[1,2] and cyclopropanation reactions.[3] Nickelacyclobutane complex 1 is believed to be in equilibrium with olefin-coordinated nickel-carbene complex 2 on the basis of the available experimental evidence (eq. 1)[1,2]. In this communication, some new reactions of nickel-carbene complexes with H_2 and CO will be reported.



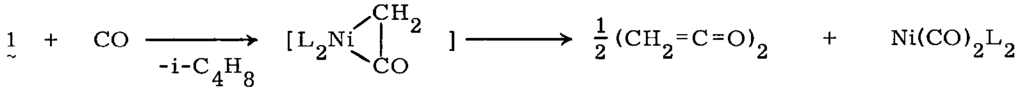
1

2

$L=P(C_6H_5)_3$

(1)

When 1 in toluene was pyrolyzed in the presence of H_2 by raising the temperature from -50 °C to 50 °C, methane, 2-methylpropane, 1,1-dimethylcyclopropane, and 2,2-dimethylpropane were produced in 32% (per Ni), 37%, 19%, and 8% yield, respectively. In the absence of H_2, it decomposed on heating at 49 °C to give ethylene (15%), 2-methylpropene (26%), 1,1-dimethylcyclopropane (47%), 3-methyl-1-butene (6%), and 2,2-dimethylpropane (6%). The origin of the hydrogen atoms in the conversion of carbene species of 2 to methane was established to be an added H_2 by deuterium labeling experiments; by replacing H_2 by D_2 were obtained methane-d_2 and 2-methylpropane-d_2 of satisfactory isotopic purities.[4] The absence of 2,2-dimethylpropane reflects that the species 2 appears to be more kinetically labile toward H_2 than the metallacyclobutane 1. The reaction of 1 with CO resulted in the formation of ketene dimer (11%) and 2-methylpropene. No cyclobutanones were obtained. The reaction is most reasonably interpreted in terms of a nucleophilic attack of the carbenic carbon in 2 to the coordinated CO molecule to form nickel-ketene complex 3.[5] Attempted methylene transfer to



3

$L=P(C_6H_5)_3$

(2)

acetone or diphenylmethylphosphine failed.[6]

Carbon monoxide was converted into ethanol (14% per Ni) by the reaction with **1** in the presence of H_2 followed by hydrolysis. Two deuteriums were incorporated into ethanol when the reaction was carried out in the presence of D_2, indicating that the reaction proceeds via **3**

$$\mathbf{1} \quad + \quad CO \quad + \quad H_2 \quad \longrightarrow \quad C(CH_3)_4 + CH_4 + i\text{-}C_4H_8 + C_2H_5OH \qquad (3)$$

followed by successive hydrogenation to alcohol. The above results suggest that other Fischer-Tropsch type reactions may also proceed by way of metal-ketene complexes.[7]

Nickelacyclohexane complex which was reported to generate nickel carbene complexes[1,2] was allowed to react with CO to yield cyclohexanone (62%) as a mojor product in addition to ketene dimer (up to 6%). By contrast, no experimental evidence of the formation of carbenoid species in palladium[2] or platinum[8] analog was obtained throughout the reaction with H_2 or CO.

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(4) Isolated by glc. The isotopic purity was determined by mass spectroscopy. The accuracy of these determination varied with the sample, but was within ± 4%.

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